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Experimental study of stabilization of sludge containing toxic metal by hydraulic binders

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Abstract

Heavy metals term implying a concept of toxicity, among these elements: vanadium, chromium, cobalt, nickel, copper, arsenic, selenium, cadmium, mercury, etc. In addition, stabilization is defined like the process which makes it possible to reduce the dangerous potential and lixiviability of a material (waste, ground, etc.) by converting these contaminants in less soluble forms, mobiles or toxics.

The concept of stabilization is often associated with the concept of solidification; we always find the term stabilization/solidification (S/S). Solidification makes it possible to transform a material into one monolith solid having a good physical integrity and structurally homogeneous. Solidification inevitably does not imply chemical reaction between the waste and the agent of solidification: that can be a mechanical trapping of waste in the solid. In the same way for stabilization, who can only be one modification of environment (like a change of pH). The objective of our study is to find a solution with solid waste produced from shovels and cranes complex (Ain Smara Constantine, Algeria) (CPG) who are represented by great quantities of sludge charged mainly of trivalent chromium (after reduction of Cr(VI)). We tried to stabilize or solidify toxic metal by a hydraulic cement at the cement factory (Hamma Bouziane, Constantine, Algeria); the experiments which were carried out on the level of the complex (CPG) are: determination of the content of hexavalent chromium before and after treatment (liquid phase), and determination of the chromium quantity contained in produced sludge by fluorescence X-rays. On the level of the cement factory, we carried out the chemical analyses (determination of oxides…), with the mechanical tests and physics on pure cement, cement and sludge (container of chromium); and the mixture before cooking vintage "Cru" and sludge (charged of chromium). In addition, we tried to act upstream by adsorption of Cr (VI) before its reduction in Cr(III) to recover it while reducing thus quantity of produced sludge.

Keywords: Adsorption, Heavy metals, Chrome, Stabilization, Solidification, X-rays, UV-Visible.

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1. Introduction

There are five great strategies of management of the industrial waste [1]. Both first the stop of the production of a given waste and the optimization of the process of which it is resulting, aim at a reduction of the quantity of produced waste. The two following ones have for objective to treat waste, it is of recycling or the re-use and of the rejection. They are addressed to waste of which the quantity was reduced or with "irreducible'' by the first two ways. Not only these four strategies do not make it possible to manage all waste but they inevitably result in generating secondary waste. The last strategy consists in storing. It is addressed to primary excluded waste and with secondary waste resulting from the four preceding ones [2].

Waste not having initially the characters of massivity and stability must undergo a treatment known as stabilisation/solidification, generally requiring the use of binders materials [3].

Although the methods of stabilization can sometimes be used for industrial waste [4], stabilization with the hydraulic binders is one of the most current methods to stabilize and solidify various industrial waste containing heavy metals (like metal sludges) [5].

The objective of our work is to solve the problem of sludge containing Trivalent Chromium produced from shovels and cranes complex (CPG Ain Smara) by introducing it like addition (in very small quantity) with the cementing matrix.

2. Use of chromium in shovels and cranes complex (CPG)

Chromium is a good oxidant, it hardens steel and facilitates the forging of metal; with low content it does not prevent its weldability. Chrome steels are harder than carbon steels.

The property of chromium is to increase considerably the elasticity of steel and to communicate it a particular resistance to the shock, but its fundamental property is to support the hardening penetration. Also, it is possible to obtain parts large thickness misled. It increases also the transformation point of heating and involves a rise in the temperature. Complex waste water (in CPG) are resulting from chromium plating baths.

During the treatment, water contaminated by chromium sudden a reduction by addition of sodium bisulfit according to the reaction :

$$6NaHSO_3 + 4H_2CrO_4 + 3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 \longrightarrow \quad + 3Na_2SO_4 + 10H_2O \qquad (1)$$

After reduction of hexavalent chromium, water is neutralized by NaOH. The produced sludge is stocked in specific surfaces.

3. Origin of cement

The generic term cement indicates in fact various categories of products. A category is defined by its composition and classes characterizing the mechanical resistances arrivals in the given term. Cement known as Portland, because of analogy of its composition with that of the stone of Portland, is most current. It is made up mainly of clinker, resulting from cooking until partial fusion (towards 1450°C) then crushing of a mixture of rocks limestones and argillaceous [6].

- Artificial Portland cements or CPA-CEM I containing at least 97% of clinker and calcium sulphate (gypsum) like regulator of catch;

- Portland cements with secondary components or CPJ-CEM II containing more 65% of clinker (secondary components, fine powders resulting from rocks, are inert or active from the hydraulic point of view).
To define the various components of cement, we will use their notation which is as follows : C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, S = SO_3 and H = H_2O.
Ordinary Portland cement is composed of four major phases : 40 to 60 % alite (tricalcic silicate - C_3S) ; 15 to 30 % belite (bicalcic silicate - C_2S) ; 5 to 15 % of celite (tricalcic aluminate - C_3A) ; and 5 to 15 % of ferrite (ferroaluminate tetracalcic - C_4AF). There are various types of Portland cements.

4. Materials and method

Different mixtures cement-sludge, vintage–sludge, are realized in cement factory, cooking of the mixture is assured in a laboratory furnace; different analysis, chemical physics and mechanics are also realized at the same laboratory.

Batch adsorption experiments were carried out in Erlenmeyer flasks of 1000 ml capacity installed on the thermostatic magnetic stirrer. The pH values were measured by a pH-meter. The Chromium (VI) solutions was prepared by dissolving chromium trioxide (CrO_3) in distilled water. Standard solutions of 0.5 N HCl and NaOH were used to adjust the pH of solution. For each sample, the adsorbent was separated from the solution by filtration. The filtrate is analysed by spectrophotometry UV-Visible method, with a wave length of 540nm; in this part the important parameters studied are pH of medium and initial concentration of chromium.

5. Results

5. 1. At shovel and crane complex (CPG)

5.1.1. Content of Cr(VI) and Cr(III) before and after treatment

At CPG complex, the determination of chromium (Cr(VI) and Cr(III)) before and after treatment is carried out, the results are presented in table 1.

Table 1. Measurement of Cr(VI) and Cr(III)

	Cr(VI)	Cr(III)
Before treatment	114 mg/l	00 mg/l
After treatment	00 mg/l	00 mg/l

Procedure of the water treatment at CPG is to reduce chromium (VI) to chromium (III) (less toxic), this last is eliminated by precipitation in the hydroxides form. Sludge thus obtained containing chromium (III).

5.1.2. Analyze of Sludge by X-ray fluorescence

In order to know the various significant elements which can exist in sludge, the determination of these elements is carried out by x-ray fluorescence, the results obtained are presented in the following table :

Table 2. Results of analysis by x-ray fluorescence of sludge

Element	Percentage (%)
Mg	0.435
Al	0.37
Si	3.281
P	1.014
S	3.902
Ca	8.64
Cr	37.174
Fe	15.15
Zn	0.708

Sludge analysed by x-ray fluorescence shows that the latter is very charged with trivalent chromium.

5.2 In the cement factory

In this part, the experimental results carried out in the cement factory are presented, as known chemical analysis and physical tests. In the experiments, the procedure is to mix the vintage (limestone + clays: red (high quantity of Silica) and brown (high quantity of alumina)) with very small quantities of sludge containing chromium.

5.2.1 Sludge analysis

In order to know the various significant components of cement which can exist in sludge, we sought the content of these elements by fusion and then by volumetric titration in the cement factory.

Table 3. Results of sludge analysis

	Sludge %
CT (chemical title)	2.01
SiO_2	6.79
CaO	8.39
Fe_2O_3	11.39
Al_2O_3	2.84
MgO	0.98
PAF	31.31

PAF: loss on fire

According to the results obtained it notes that sludge cannot be used as raw material because it is low in lime (CaO) and silica (SiO_2), on the other hand it can be used as addition or like a matter of correction.

5.2.2 Analysis of the mixture cement-sludge

Same chemical stages of analysis, physical and mechanical tests were followed for various percentages of sludge mixed with cement.

- Chemical analysis

Results obtained are summarized in the table 4.

Table 4. Influence of sludge on the cement components

	Cement +5% sludge	Cement + 3% sludge	Cement + 1.5% sludge	Cement +1% sludge	Cement +0% sludge
PAF (%)	04.61	04.40	04.14	04.13	03.98
CaO free(%)	00.09	00.09	00.09	00.09	00.09
CaO (%)	55.60	55.90	56.58	56.58	57.16
Fe_2O_3(%)	02.78	02.78	02.50	02.50	02.50
Al_2O_3(%)	04.26	04.26	04.43	04.61	04.61
MgO(%)	01.54	01.26	00.98	00.98	01.26
SiO_2(%)	27.57	27.98	28.22	28.22	28.24
SO_3(%)	02.24	02.06	01.38	01.28	01.31
Insoluble(%)	10.30	09.97	09.65	09.43	09.30

Increase in the percentage of sludge in the cement bringing to a weak reduction percentage of the major elements (CaO, Fe_2O_3, Al_2O_3, SiO_2). An increase in the percentage of insoluble, of SO_3 and of PAF was marked. The free lime (CaO) is almost constant with different percentages added of sludge. In conclusion, it can be see that the sludge addition containing chromium does not have much influence on flexible qualities of cement.

- *Mechanical and physical tests*

With an aim to check if addition of sludge has influence especially on resistances of cement, mechanical and physical tests are carried out.

- *Mechanical tests*

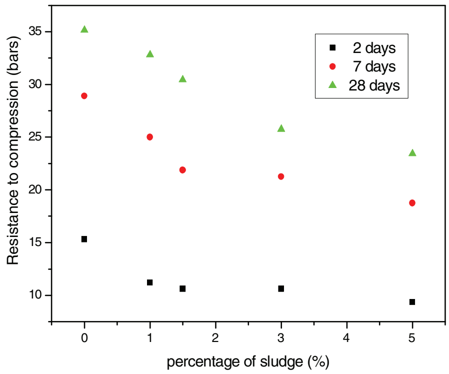

Fig. 1. Variation of compression resistance with different percentages of added sludge

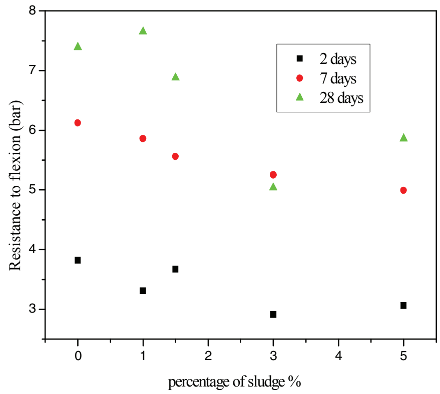

Fig. 2. Variation of flexion resistance with different percentages of added sludge

According to Figure 1, it notes that the value of the compression resistance decreases with the percentage of sludge in 2 , 7 and 28 days; that it can be due to the bad homogenisation of the mixture, or to the connection C-S-H (responsible for obtaining good resistances) which is not formed, that it can be caused by the adsorption of sludge of a certain quantity of water.

Figure 2 shows the variation of flexion resistance with different percentages of added sludge, it is noted that we obtain the same variations of flexion resistance compared with compression resistance , at 1.5% of sludge addition and at 2 days duration, the flexion resistance is almost identical to that of 0% of sludge addition for the same duration.

- *Physical tests*

In this part, we present some experiments of the physical tests which were carried out on cement mixed with a certain quantities of sludge; the results were recapitulated in the table 5:

Table 5. Influence of addition of sludge on physical tests of cement

Percentage of sludge in cement	5 %	3 %	1.5 %	1%	0 %
Beginning catch of cement (min)	199.00	181.00	185.00	188.00	192.00
End of catch of cement (min)	267.00	249.00	253.00	245.00	228.00
Hot expansion (mm)	00.00	01.00	00.00	01.00	00.00
Blaine test (SSB) cm^2/g	3379	3450	3475	3500	3516

A Blaine test is used for determining the fineness of cement, or other fine material, on the basis of the permeability to air of a sample of the material prepared under specified conditions. According to the results obtained it is noted that times of the catches are delayed in the case of cement with sludge that in cement without sludge for end of catch. On the other hand in the case of beginning of catch, a weak reduction in time is marked for an addition of sludge varying from 1 to 3%, whereas with

5% of addition time is delayed of 7 min. In this case sludge takes the same role of the gypsum. Increase in the percentage of sludge cause a reduction in SSB thus sludge influences on the smoothness of cement.

5.2.3. Case of the mixture vintage – sludge

In this case, the addition of sludge is done with vintage, before cooking, the experimental results obtained are compared with a cooking of the vintage without addition of sludge.

a) Analyses of the pure clinker (without addition of sludge)

Same stages are used for cement analysis. Results are presented in the table 6.

Table 6. Percentages of various components of the clinker

	Pure clinker %
SiO_2	21.37
CaO libre	01.50
CaO	68.28
Fe_2O_3	02.59
Al_2O_3	05.50
MgO	01.26
PAF	00.22
Insolubles	00.24

According to Table.6, it is noted that it is a good clinker because it contain large quantity of CaO and SiO_2.

b) Clinker obtained by mixture of vintage and sludge

99% of the vintage are mixed with 1% of sludge and cooking were carried out at 1450°C during 1/2 hour in the laboratory furnace, this operation is called clinkerisation. After clinkerisation and crushing, the chemical analysis, physical and mechanical tests were made to obtain the clinker components.

- Chemical analysis

The results of chemical analysis for determination of the clinker components are presented in table.7

Table 7. Results of the chemical analyses of the clinker

	Our clinker %	Pure clinker %
Free lime $(CaO)_l$	04.65	01.50
PAF	00.50	00.22
SiO_2	22.00	21.37
Insoluble	00.40	00.24
CaO	67.89	68.28
Fe_2O_3	02.50	02.59
Al_2O_3	05.50	05.50
MgO	0.98	01.26

According to table 7**,** and after comparison between our clinker (with 1% of sludge) and the pure clinker it is noted that the percentages of CaO, Fe_2O_3, Al_2O_3, SiO_2, MgO, PAF and the insolubles are almost the same; except that, there is a certain increasing in free lime, which can be explained by:

1. bad cooking which leads to an incomplete combination of C_2S and CaO and thus release of CaO not combined in the form of free CaO ;
2. an incorrect hardening which leads to a decomposition of C_3S to C_2S and free CaO;
3. a lack of the variation in temperature ;
4. bad homogenisation ;

- Mineralogical compositions and chemical modules

The chemical modules and the mineralogical compositions are calculated by the method of BOGUE who allows to judge cooking. These calculations are carried out starting from the chemical analysis of the clinker.

Table 8. chemical modules and the mineralogical composition

	Our clinker %	Pure clinker %
C_3S	68.58	74.82
C_2S	11.70	10.12
C_3A	10.35	10.19
C_4AF	07.60	07.87
MS	02.75	01.50
IM	02.20	02.12
FSC	97.38	100.00
Δ	1.825	- 00.27

MS: Silicic module, IM: aluminoferric module, FSC: Factor of saturation, Δ : difference between real and theoretical lime.

The experimental results obtained are presented in table 8; by comparison of our clinker (obtained by mixture of vintage with the sludge containing of chromium) with the pure clinker, It is noted that the obtained results are acceptable.

5.2.4 Cement obtained by addition of the important component

In this part, cement is prepared by : 5 % of gypsum, 13 % of tuff and 82 % of clinker (obtained by addition of vintage and a certain quantity of sludge containing chromium).

- *Chemical analysis*

Table 9. Results of the chemical analysis of our cement

	Cement + sludge (%)	Pure cement (%)
CaO_l	04.50	00.09
PAF	01.98	03.98
SiO_2	23.73	28.24
Insolubles	08.43	09.30
CaO	57.75	57.16
Fe_2O_3	02.50	02.50
Al_2O_3	05.32	04.61
MgO	00.98	01.26
SO_3	02.59	01.31

According to the results obtained in the Table 9, it is noted that a good cement is obtained which can give fine resistances.

- *Mechanical tests*

Table 10. Results of the mechanical tests

Resistance	2 days	7 days	28 days
to flexion (our cement) (bar)	02.49	04.59	05.89
to flexion (cement of company) (bar)	03.82	06.12	07.39
to compression (our cement) (bar)	08.75	18.75	29.00
to compression (cement of company) (bar)	15.31	28.90	35.15

According to the results presented in table 10, it is noted that there is a certain difference between the compression and flexion resistances of our cement (cement + sludge) compared with cement of the company, this difference can be explained again by :

1. bad cooking which leads to an incomplete combination of C_2S and CaO and thus release of CaO not combined in the form of free CaO ;
2. an incorrect hardening which leads to a decomposition of C_3S to C_2S and free CaO ;
3. a lack of the variation in temperature;
4. bad homogenisation ;

5.3 Adsorption of Cr(VI) on activated carbon

With an aim of reducing the quantity of sludge produced in CPG, we tried to recover a certain quantity of chromium (VI) by adsorption on activated carbon in agitated reactor [7].

- *Influence of pH and initial concentration of CrO_3*

Operating conditions :

$m_{\text{activated carbon}}$=1g, Agitation=500 tours/min, T=20°C

In acidic medium, the reduction in the quantity of Cr(VI) is considerable compared with the neutral and alkaline mediums(figure 3), it is to be announced that the activated carbon adsorbs better in the acid media.

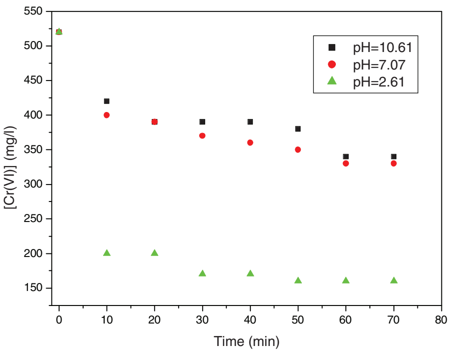

Fig. 3. Variation of the quantity of Cr(VI) with time at different pH

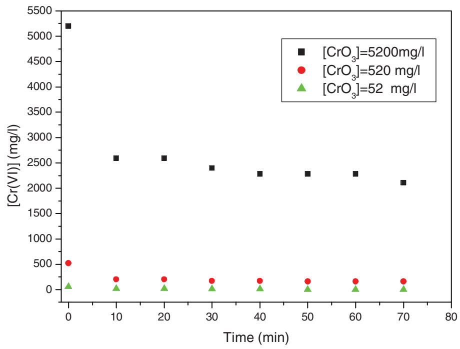

Fig. 4. Variation of the quantity of Cr(VI) with time at different concentrations of CrO_3

According to figure 4, it is seen that elimination is very significant between 0 and 10 minutes in the case of 5200 mg/l compared with others cases (520 et 52 mg/l), thus for a more quantitative elimination of chromium, it is necessary to increase the quantity of the activated carbon.

6. Conclusion

This experimental work has been realised in first part at CPG (Complexe Pelles et Grues Ain Smara, Constantine Algeria) to determine chromium quantity present in sludge, in other part at laboratory of cement factory (Hamma Bouziane, Constantine, Algeria) to test different addition percentage of sludge to the clinker or cement. The main result shows that we can add a small quantity of sludge (1%) with the cilnker of the company thus involves a small modification of resistances to flexion and compression of cement.

To supplement the study, it is significant to carry out the analysis of the gas phase to see the presence or not of Cr(III) among the flaring gases. The best way to minimize the production of sludge in the complex (CPG) is to recover chromium (VI) by adsorption on activated carbon followed by a desorption ; the results obtained show that a great recovery of Cr(VI) is possible at weak pH.

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